

Patent Claims

1. Recycling-pickling method for copper and copper alloys, characterized in that:
 - a sulfuric-acid iron-III sulfate solution with or without peroxodisulfates is utilized for pickling,
 - the spent solution is regenerated in one or in several regeneration electrolytic cells partitioned by ion exchanger membranes or porous diaphragms, so that the dissolved copper is precipitated cathodically and the iron-III sulfate is regenerated anodically and optionally peroxodisulfate is formed,
 - the thus-regenerated pickling solution enriched with oxidation agent is introduced into the pickling bath for oxidation to a higher state and for adjustment of a pregiven redox potential.
2. Method according to claim 1, further characterized in that a sulfuric-acid base pickling solution that is cycled is used, which contains 0.1 to 6 moles/liter sulfuric acid, 0.1 to 0.5 moles/liter of copper sulfate and 0.1 to 1 mole/liter iron sulfates as well as also 0 to 2 moles/liter alkali or ammonium sulfates and/or sulfates of other dissolved metals, such as, e.g., nickel, zinc, etc.
3. Method according to claims 1 and 2, further characterized in that the redox potential in the pickling bath (measured against a silver/silver chloride

reference electrode) is adjusted to values between 300 and 1150 mV, adapted to the requirements of the material composition to be pickled, by metering in the regenerated pickling solution containing iron-III sulfate and peroxodisulfate.

4. Method according to claims 1 to 3, further characterized in that a peroxodisulfate electrolytic cell that is partitioned by ion exchanger membranes is used as the regeneration electrolytic cell, and a partial flow of the pickling bath to be regenerated is metered into this cell and the latter first passes through the cathode spaces for the reduction of the residual iron-III sulfate and for the precipitation of metallic copper and then passes through the anode spaces for the reoxidation to iron-III sulfate and optionally for enrichment with peroxodisulfate.
5. Method according to claims 1 to 4, further characterized in that the peroxodisulfate electrolytic cell is furnished with a catholyte circuit by means of a separating device, in which the copper cathodically precipitated in powder form is separated.
6. Method according to claims 1 to 5, further characterized in that a metal-recovery electrolytic cell partitioned by ion exchanger membranes or diaphragms is utilized as the regeneration electrolytic cell, in which, in addition to the reduction of excess iron-III sulfate, copper is precipitated cathodically in compact form and recovered, whereas, iron-II sulfate is reoxidized anodically to iron-III sulfate.

7. Method according to claims 1 to 6, further characterized in that both a metal-recovery electrolytic cell as well as a peroxodisulfate electrolytic cell are utilized for regeneration and the pickling solution to be regenerated is first freed of excess iron-III sulfate as well as optionally of peroxodisulfate by addition of copper powder, and then the principal quantity of copper is precipitated in compact form in the cathode spaces of the metal-recovery electrolytic cell, and then is fed into the catholyte circuit of the peroxodisulfate electrolytic cell, where the precipitated powder is discharged and is fed back for the breakdown of the excess iron-III sulfate, while the discharged catholyte sequentially passes through the anode spaces of the metal-recovery electrolytic cell and the peroxodisulfate electrolytic cell for the reoxidation to iron-III sulfate and peroxodisulfate, and is again metered into the pickling bath for maintaining the previously adjusted redox potential.
8. Method according to claims 1 to 7, further characterized in that a larger partial flow is transported directly over the anode spaces of the metal-recovery electrolytic cell and from there again to the pickling bath for the regeneration of the pickling bath, while a smaller partial flow is sequentially transported through the cathode spaces of the metal-recovery cell and the peroxodisulfate electrolytic cell as well as over the anode spaces of the peroxodisulfate electrolytic cell again into the pickling bath.
9. Method according to claims 1 to 8, further characterized in that the peroxodisulfate content of the regenerated pickling solution is increased to

values between 0.1 and 1 mole/liter in the peroxodisulfate electrolytic cell and this solution is intermediately stored in order to increase for a short time the redox potential from a lower level to a pregiven higher level by metering this solution into the pickling bath.

10. Method according to claims 1 to 9, further characterized in that a redox potential between 500 and 700 mV (against Ag/AgCl) is established in the pickling bath for the pickling of copper, brass and bronzes as well as copper alloys with small additions of nickel, cobalt, iron, lead, beryllium, phosphorus, silicon and zirconium.
11. Method according to claims 1 to 9, further characterized in that a redox potential between 700 and 1150 mV (against Ag/AgCl) is established in the pickling bath for the pickling of copper-nickel alloys with nickel contents of more than 10%.
12. Method according to claims 1 to 9, further characterized in that a redox potential between 300 and 500 mV (against Ag/AgCl) is established in the pickling bath for the pickling of copper alloys with the alloy components tellurium and sulfur.
13. Method according to claims 1 to 9 and 12, further characterized in that a larger partial flow of the solution to be regenerated is transported only over the cathode spaces of the metal recovery cell and from there directly back into the pickling bath, whereas a smaller partial flow, after passing through the cathode spaces of the peroxodisulfate electrolytic cell, sequentially

passes through the anode spaces of the metal-recovery cell and the peroxodisulfate electrolytic cell, is reoxidized anodically therein, and is enriched with peroxodisulfate and is intermediately stored for the short-term increasing of the redox potential to a higher level.

14. Method according to claims 1 to 13, further characterized in that known additives such as activators, inhibitors and/or complexing agents are metered into the cycled pickling solution.
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